Anomalous Rotational Relaxation:
A Fractional Fokker-Planck Equation Approach

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In this study we obtained analytically relaxation function in terms of rotational correlation functions based on Brownian motion for complex disordered systems in a stochastic framework. We found out that rotational relaxation function has a fractional form for complex disordered systems, which indicates relaxation has non-exponential character which obey to Kohlrausch-William-Watts law, following the Mittag-Leffler decay.

Relaxation for ordered systems is given by Maxwell-Debye law [1, 2] as

$$\Phi\left(t\right) = \Phi_0 \exp\left(-t/\tau\right), \quad t \geq 0. \tag{1}$$

Whereas, relaxation in many complex disordered systems such as metallic glasses, spin glass alloys [3, 4, 5, 6], ferroelectric crystals [7], dielectrics [8] deviates from the classical exponential Maxwell-Debye pattern and is often described in terms of Kohlrausch-William-Watts (KWW) (i.e. stretched exponential) law [8, 9],

$$\Phi\left(t\right) = \Phi_0 \exp\left(-t/\tau\right)^\alpha \tag{2}$$

for $0 < \alpha < 1$, or by an asymptotic power-law

$$\Phi\left(t\right) = \Phi_0 \left(1 + t/\tau\right)^{-n} \tag{3}$$

with $n > 0$. The relaxation functions in Eqs.(1) and Eq.(2) are commonly written in terms of the correlation functions which correspond to decay of the fluctuation of the a physical quantity such as magnetization in magnetic materials, polarization in the dielectric materials.

Relaxation function has been derived using rotational relaxation method for some system. This method has been firstly used by Debye in the context of dielectric relaxation of polar molecules [2]. The same picture has been applied to the rotational motion of the magnetization vector of a super-paramagnetic particle [10], the polarization vector of a polar molecule in a dielectric [11], and heavy molecules [12, 13] in the liquid and gases.

The relaxation functions Eqs.(1) and (2) are written in terms of correlation functions. Our main aim, in this study, is obtain relaxation function Eq.(2) for some complex disordered systems in terms of rotational correlation functions based on rotational Brownian motion in a stochastic framework.

The most common calculation in which the picture of rotational Brownian motion finds relevance is that of the rotational correlation function $\Phi_l^R\left(t\right)$, which can be measured by Infrared (IR) and Raman (R) spectroscopies as well as the neutron and ultrasonic scattering techniques

[14]. Correlation function $\Phi_l^R\left(t\right)$ measures the correlation in time between the direction of the unit vectors (defining the molecular symmetry axis) $\mathbf{u}(0)$ and $\mathbf{u}(t)$. Therefore, $\Phi_l^R\left(t\right)$ as can be obtained from the IR and Raman spectroscopies may be expressed in the compact form,

$$\Phi_l^R\left(t\right) = \langle P_l\left(\mathbf{u}\left(0\right).\mathbf{u}\left(t\right)\right)\rangle \tag{4}$$

where $\mathbf{u}$ is the unit vector along the symmetry axis of the molecule, and P_l is the Legendre polynomial of order l. Argument of P_l is expressed as $\mathbf{u}\left(0\right).\mathbf{u}\left(t\right) = \cos\gamma\left(t\right)$, where γ is angle between two different point at the spherical coordinate system. These points are given by (θ_0, ϕ_0) and (θ, ϕ) which denote two different directions by separated by an angle γ. There angles satisfy the trigonometric identity,

$$\cos\gamma = \cos\theta_0 \cos\theta + \sin\theta_0 \sin\theta \cos\left(\phi_0 - \phi\right) \tag{5}$$

The addition theorem asserts that

$$P_l\left(\cos\gamma\right) = \frac{4\pi}{2l+1} \sum_{m=-l}^{l} Y_l^m\left(\theta_0, \phi_0\right) Y_l^{m*}\left(\theta, \phi\right). \tag{6}$$

If we inserted Eq.(6) into Eq.(4) rotational correlation function is expressed in general form using spherical harmonics addition theorem as

$$\Phi_l\left(t\right) = \frac{4\pi}{2l+1} \sum_{m=-l}^{l} \langle Y_l^m\left(\Omega_0\right) Y_l^{m*}\left(\Omega\left(t\right)\right)\rangle. \tag{7}$$

Such a theoretical approach allow us to calculate for arbitrary l. Average in Eq.(7) is calculated over the probability density functions of Brownian particle which refers to end of point polarization vector or a real particle. The Brownian motion in disordered space in the presence of an external field $F(x) = -V'(x)$ leads to Fractional Fokker-Planck Equation (FFPE) [15, 16, 17, 18, 19]:

$$\frac{\partial}{\partial t} W\left(x_0, 0 \mid x, t\right) = {}_0 D_t^{1-\alpha} L_{FP} W\left(x_0, 0 \mid x, t\right) \tag{8}$$

$$L_{FP} = \left[\frac{\partial}{\partial x} \frac{V'(x)}{m\eta_\alpha} + K_\alpha \frac{\partial^2}{\partial x^2} \right] \qquad (9)$$

This equation then characterize sub-diffusion process. The FFPE are closely related generalized Lévy-type statistics [20] and can be derived from continuous time random walk (CTRW) models [21, 22, 23, 24, 25, 26], or from a Langevin equation [27]. In Eq.(8), $W(x_0, 0 \mid x, t)$ imply conditional probability for Brownian motion, m denotes mass of the particle, K_α the diffusion constants associated with the transport process, and the friction coefficient η_α is a measure for interaction of the particle with its environment. The coefficient is given as $K_\alpha = k_B T/m\eta_\alpha$. K_α is a generalization of the Einstein-Stokes-Smoluchowski relation [15, 16, 17, 18, 19] which holds for the generalized coefficient η_α. In the Eq.(8) operator $_0D_t^{1-\alpha}$ is known fractional Riemann-Liouville integro-differential operator [28].

The fractional Riemann-Liouville operator $_0D_t^{1-\alpha} = \frac{d}{dt}\,_0D_t^{-\alpha}$ featuring is defined through

$$_0D_t^{1-\alpha}W(\theta_0, \phi_0, 0 \mid \theta, \phi, t) = \frac{1}{\Gamma(\alpha)}$$
$$\times \frac{\partial}{\partial t} \int_0^t dt' \frac{W(\theta_0, \phi_0, 0 \mid \theta, \phi, t)}{(t-t')^{1-\alpha}} \qquad (10)$$

The fractional integro-differentiation operator $_0D_t^{1-\alpha}$ contains a convolution integral with a slowly decaying power-law Kernel $M(t) = \frac{t^{\alpha-1}}{\Gamma(\alpha)}$, ensures the non-Markovian nature of the sub-diffusion process defined by the fractional diffusion process. Its fundamental property is the fractional integro-differentiation of a power,

$$_0D_t^{1-\alpha}t^p = \frac{\Gamma(1+p)}{\Gamma(p+\alpha)}t^{p+\alpha-1} \qquad (11)$$

In fact, it can be shown that more general relation

$$_0D_t^p t^q = \frac{\Gamma(1+q)}{\Gamma(1+q-p)}t^{q-p} \qquad (12)$$

for any real p, q. Thus, the fractional derivative of a constant,

$$_0D_t^q 1 = \frac{1}{\Gamma(1-q)}t^{-q}, \quad q > 0 \qquad (13)$$

reproduces an inverse power-law. The special cases of integer order integro-differentiation of a constant, $\frac{d^n 1}{dt^n} = 0$, are included through the poles of the Gamma function for $q = 1, 2, 3, \dots$.

In the case of $V'(x) = 0$ which means that there is no an external field, the one-dimensional FFPE can be reduced to diffusive type equation;

$$\frac{\partial}{\partial t}W(x_0, 0 \mid x, t) = _0D_t^{1-\alpha}K_\alpha\frac{\partial^2}{\partial x^2}W(x_0, 0 \mid x, t). \qquad (14)$$

This equation is called fractional diffusion equation [29, 30, 31] which is a particular form of the FFPE which can be represent on the spherical coordinates as a function of the angles θ and ϕ as

$$\frac{\partial}{\partial t}W(\theta_0, \phi_0, 0 \mid \theta, \phi, t) = _0D_t^{1-\alpha}d_\alpha\nabla^2 W(\theta_0, \phi_0, 0 \mid \theta, \phi, t) \qquad (15)$$

where d_α is referred to as the rotational diffusion constant that is related to translational diffusion constant K_α and the radius a by $d_\alpha = K_\alpha/a^2$ ($a = unit$)

$$\nabla^2 = \frac{1}{\sin^2\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right] \qquad (16)$$

The standard method of solution of Eq.(15) is the separation variables [15, 16, 17, 18, 19]. If we consider separation ansatz, we have obtained the two eigen-equations as

$$\frac{dT(0 \mid t)}{dt} = -\lambda^2 d_\alpha {}_0D_t^{1-\alpha}T(0 \mid t) \qquad (17)$$

$$\nabla^2 Q(\theta_0, \phi_0 \mid \theta, \phi) = -\lambda^2 Q(\theta_0, \phi_0 \mid \theta, \phi) \qquad (18)$$

The temporal eigen-equation Eq.(17) is but the fractional relaxation equation, the solution of which is given in terms of the Mittag-Leffler function [32]

$$T(0 \mid t) = E_\alpha\left[-d_\alpha l(l+1)t^\alpha\right] \equiv \sum_{j=0}^\infty \frac{\left[-d_\alpha l(l+1)t^\alpha\right]^j}{\Gamma(1+\alpha j)}. \qquad (19)$$

As can be seen from the series expansion, the exponential form can be recovered in the Brownian limit $\alpha = 1$

$$E_1\left[d_1 l(l+1)\ t^1\right] = \exp\left[d_1 l(l+1)\ t\right]. \qquad (20)$$

This result indicates that for $\alpha = 1$ Mittag-Leffler relaxation modes leads to Maxwell-Debye pattern, on the other hand, for interval $0 < \alpha < 1$ Mittag-Leffler function indicates non-Markovian Brownian motion.

On the other hand, a convenient way of expressing solution of the spatial eigen-equation Eq.(18) is by means of spherical harmonics

$$Q(\theta_0, \phi_0 \mid \theta, \phi) = \sum_{l=0}^\infty \sum_{m=-l}^l \frac{4\pi}{2l+1}Y_l^m(\theta_0, \phi_0)Y_l^{m*}(\theta, \phi). \qquad (21)$$

As a result, if solutions Eqs.(19) and (21) are inserted into Eq.(15), it is obtained the conditional probability for Brownian particle in terms of Mittag-Leffler function

$$W(\theta_0, \phi_0, 0 \mid \theta, \phi, t) = \sum_{l=0}^\infty \sum_{m=-l}^l \frac{4\pi}{2l+1}Y_l^m(\theta_0, \phi_0)$$
$$\times Y_l^{m*}(\theta, \phi)E_\alpha\left[-d_\alpha l(l+1)\ t^\alpha\right] \qquad (22)$$

Eq.(22) can be written as a compact in terms of the Euler angles $\Omega_0 (\theta_0, \phi_0)$ and $\Omega (\theta, \phi)$, hence

$$W (\Omega_0, 0 \mid \Omega, t) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} Y_l^m (\Omega_0) Y_l^{m*} (\Omega)$$
$$\times E_\alpha [-d_\alpha l \ (\ l + 1) \ t^\alpha] \quad (23)$$

Also, Eqs.(22) and (23) should be satisfied

$$W (\Omega_0, 0 \mid \Omega, 0) = \delta (\Omega_0 - \Omega) \quad (24)$$

for $t = 0$.

It is easy give the correlation function Eq.(7) what is by now a familiar interpretation as

$$\Phi_l (t) = \frac{4\pi}{2l+1} \sum_{m=-l}^{l} \int w (\Omega_0) Y_l^m (\Omega_0)$$
$$\times W (\Omega_0, 0 \mid \Omega, t) Y_l^{m*} (\Omega) \, d\Omega_0 d\Omega. \quad (25)$$

In above equation $w (\Omega_0)$ is a priori probability that the initial orientation is given by Ω_0, while $W (\Omega_0, 0 \mid \Omega, t)$ is the conditional probability that the final orientation is determined Ω. Assuming that the reorientations of the spin (or molecular) symmetry axis may be modelled as an isotropic rotational Brownian motion, we may write

$$w (\Omega_0) = 1/4\pi \quad (26)$$

and adopt Eq.(23) as the solution for the conditional probability by replacing l with l', and m with m' respectively. Hence Eq.(24) yields,

$$\Phi_l (t) = \frac{4\pi}{2l+1} \sum_{m=-l}^{l} \sum_{l'm'} \left(\frac{1}{2l'+1} \right)$$
$$\times E_\alpha [-d_\alpha l' \ (\ l' + 1) \ t^\alpha]$$
$$\times \int Y (\Omega_0) Y_{l'}^{m'*} (\Omega_0) \, d\Omega_0 \int Y_l^m (\Omega) Y_{l'}^{m'*} (\Omega) \, d\Omega \quad (27)$$

Using orthogonal property

$$\int Y_l^m (\Omega) Y_{l'}^{m'*} (\Omega) \, d\Omega = \delta_{ll'} \delta_{mm'} \quad (28)$$

Hence, rotational correlation function (27) is written in terms of Mittag-Leffler function [32]

$$\Phi_l (t) = \Phi_l (0) E_\alpha [-d_\alpha l (l+1) \ t^\alpha] \quad (29)$$

where normalized factor of Eq.(29) is given as $\Phi_l (0) = 4\pi/(2l+1)^2$. Eq.(29) states simply that the rotational correlation function, starting from the value unity at $t = 0$, decay non-exponentially in time with a relaxation time τ_l that inversely proportional to rotational diffusion constant d_α:

$$\tau_{\alpha,l} = [d_\alpha l (l+1)]^{-1} . \quad (30)$$

In addition, the rotational correlation function (29) is valid for arbitrary number l, and it has interesting property due to behavior of the Mittag-Leffler functions lies in the observation that is interpolates between an initial stretched exponential (i.e. KWW) behavior

$$\Phi_l (t) \approx \exp \left[-\frac{t^\alpha}{\tau_{\alpha,l} \Gamma (1 + \alpha)} \right], \quad \tau_{\alpha,l}^{-1} t^\alpha << 1 \quad (31)$$

and a long-time inverse power-law pattern

$$\Phi_l (t) \approx \left[-\frac{t^{-\alpha}}{\tau_{\alpha,l} \Gamma (1 - \alpha)} \right], \quad \tau_{\alpha,l} t^\alpha >> 1 \quad (32)$$

In conclusion, it is seen that relaxation functions Eq.(31) and (32) are compatible with Eqs.(2) and (3) for complex disordered systems, respectively.

While drafting the problem we have disregarded the inertial of free motion governed by the rotational kinetic energy among the successive collision. Indeed, the rotational Brownian motion model for complex systems make sense only when friction η_α is large i.e. the collisions are very rapid. There the rotational jumps were imagined to occur by large and arbitrary angles as opposed to the present instance in which only small-angle jumps are considered. We have obtained relaxation function in terms of rotational correlation function due to this conjecture using by generalized FFPE in absence external field at the spherical coordinates based on rotational Brownian motion.

In this letter, we have introduce generalized Fokker-Planck equations of fractional order, which generalizes the Stokes-Einstein-Smoluchowski relation, in consistency with the fluctuation-dissipation theorem. We have shown that rotational Brownian motion leads to KWW decay as known historically stretched exponential relaxation. The introduction of the Riemann-Liouville operator includes long-range memory effects which are typically found in complex systems, and consequently a single mode relaxes slowly in time, following the Mittag-Leffler decay.

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